On the Assessment and Uncertainty of Atmospheric Trace Gas Burden Measurements with High Resolution Infrared Solar Occultation Spectra from Space

M. C, Abrams[1], A, Y. Chang[2], M. R. Gunson[2], M. M. Abbas[3], A. Goldman[4], F. W. Irion[5,2] H A. Michelson[6], M, J, Newchurch[7], C. P. Rinsland[8], G. P. Stiller[9], and R. Zander[10]

Abstract. Tha Atmospheric Trace Molecule Spectroscopy km). The high spectral resolution combined with broadband (ATMOS) instrument is a high resolution Fourier transform frequency coverage allows a statistical assessment of spectrometer that measures atmospheric composition from constituent burdens from many spectral features. In the low Earth orbit with infrared solar occultation sounding in present letter, the method of analysis is discussed ● d the limb geometry. Following an initial flight in 1985,, assessed from the consistency of zonal averages of ATMOS participated in the Atmospheric Laboratory' for' observations at tropical latitudes (0-15N) relative to the Applications and Science (ATLAS) 1, 2, and 3 Space reported measurement precisions.
Shuttle missions in 1992, 1993, and 1994 yielding's total of
440 occultation measurements over a nine year period. The The ATMOS level-2 data processing retrieves vertical suite of moro than thirty atmospheric trace gases profiled profiles of atmospheric composition from the observed includes CO_2, O_3, N_2O, CH_4, H_2O, NO, NO_2, HNO_3, HCi, infrared (625-5000 cm^{-1}, or 2-16 microns) absorption HF, $ClONO_2$, CCl_3F, CCl_2F_2, CHF_2Cl, and N_2O_5. The spectra. The retrieval algorithm iteratively refines the spectroscopic error analysis is described in the context of characterization of tho state and composition of the model supporting the derived precision estimates reported with atmosphere until satisfactory agreement between the the profiles, Including systematic uncertainties astern-ad measured and calculated values Is achieved. in the ATMOS from the accuracy of the spectroscopic database. experiment, tha high spectral resolution permits the retrieval of atmospheric composition using narrow spectral windows or *microwindows* (Abrams *et al.*, 1996b provide a substantial listing of microwindows for mid-infrared trace

Introduction

Remote sensing measurements of the infrared telluric gas measurements). The selection, evaluation and spectrum sw a powerful means of studying chemical and combination Of microwindows remains a critical task in the dynamical processes in the atmosphere. The role of the definition Of a retrieval strategy; broadband high resolution ATMOS experiment as part of the shuttle-borne ATLAs 1-3 spectra offer a wide choice of spectral features suitable for missions and as a component of the NASA Mission to retrievals at different altitude levels. However, obtain ing Planet Earth has bean discussed in an accompanying Letter consistent and statistically meaningful results requires [Gunson *et* cd., 1996]. Among the current family of space careful analysis. Elements of the retrieval process have been based remote sensing experiments ATMOS is unique in presented by Norton and Rinsland [1990], Abrams *et al.*, several aspects. Tha recoverability of the instrument and the [1996a], and Abrams *et al.*, [1996b], and rely upon a self-calibrating nature of solar occultation limb sounding comprehensive database of spectroscopic parameters provide confidence in the accuracy and reproducibility of described by Brown *et al.*, [1995]. A detailed recitation of the measurements. The instrument provides spectra of high the methodology is beyond the scope of this presentation, photometric and spectral quality using a Fourier transform instead, a summary of the critical features of the processing spectrometer at a sufficiently rapid rate to profile the limb of methodology and a discussion of tha error budget will be the Barth's atmosphere with high vertical resolution (2-3 presented.

1 SAIC . NASA Langley Research Center
2 Jet Propulsion Laboratory, California Institute of Technology
3 NASA Marshall Spare Flight Center
4 University Or Denver
s California Institute Of Technology
6 Harvard University
7 University Of Alabama at Huntsville
8 NASA Langley Research Center
9 Forschungszentrum Karlsruhe/Universitaet Karlsruhe
10 Institute of Astrophysics, University or Liège

ATMOS science analysis method

The ATMOS retrieval method is a three step process of measuring temperature as a function of pressure, determining the viewing geometry, and assessing the burden of atmospheric constituents. The temperature retrieval method employed [Stiller *et al.*, 1995] provides profiles throughout the stratosphere and mesosphere with uncertainties of ~ 3-4 K, and eliminates a Potential systematic error source, A spectroscopic determination of viewing geometry, through the retrieval of the tangent pressure from the spectra in a manner that is consistent with the measurement of the trace gas burdens provides a degree of self-conalatcncy and further minimizes the potential for systematic errors [Abrams et al., 1996a]. Once the tangent pressure is assigned, the retrieval of constituent concentrations is in principle straightforward [Norton and Rinsland, 1991; Abrams et al., 1996b].

The retrieval of atmospheric trace gas concentrations is pa-formed whir an onion.peeling algorithm that models the atmosphere with 1 SO one-km *thick* homogeneous layers. Spectroscopically derived tangent pressures and a consistent temperature-pressure model are assumed and used with the ATMOS linelist compilation [Brown et al., 1995] to calculate atmospheric transmittance along a slant path at the frequency σ_i

$$T(\sigma_i, z) = \exp[-\Sigma_j \Sigma_k \kappa_{ijk} n_k x_k v_{jk} g_k] \quad (1)$$

where z is the tangent height, κ_{ijk} is the absorption coefficient for the ith spectral point due to the jth gas in the kth layer, n_k is the number density of air in the kth layer, v_{jk} is the volume mixing ratio of the jth gas in the kth layer, x_k is a multiplicative scale factor for the volume mixing ratio, and g_k is the geometrical slant path through the kth layer. The retrieval uses a least-squares fitting algorithm to scale the *a priori profile*, through the factor x, in a sequential process to fit each spectrum with a zero crossing search of the form

$$\Sigma_i [\partial T_c(\sigma_i,z)/\partial x][T_m(\sigma_i,z) - T_c(\sigma_i,z)] = 0 \quad (2)$$

where the partial derivati w of the transmission with respect to scale factor x (proportional to absorber amount) acts as a weighting function. The assumed profiles are based on the atmosphere obtained from the SPACELAB-3 mission, and the retrieval process consists of three iterative retrievals with recursive five-point polynomial smoothing between each iteration.

The uncertainty in the gas burden is directly proportional to the spectroscopic residual

$$e = v_{ink}[\Sigma_i[T_m(\sigma_i,z) - T_c(\sigma_i,z)]^2]/[N\Sigma_i (\partial T_c/\partial x)^2]^{(1/2)} \quad (3)$$

where v_{ink} is the assumed volume mixing ratio profile and N la the number of inflection points in $\partial T_c/\partial x$ (effectively the number of target gas lines within the microwindow). "ilk Immediate advantage of (3) is that it readily lends itself to the statistical combination of errors arising from individual microwindows and tends to be conservative rather than optimistic. Two additional error terms are root-sum-squared into the total measurement precision, a continuum error and a propagation error resulting from mis-estimation of the burden in previous (higher altitude) layers. These terms are usually small compared to the residual error. Typically, several microwindows are utilized in the retrieval process, with the reported profile being the weighted average over the 'n' microwindows

$$v_{wa} = (\Sigma_n v_n/\varepsilon_n^2)/(\Sigma_n 1/\varepsilon_n^2). \quad (4)$$

An estimate of the precision Of the measurement is determined two ways. The first is simply the reduced standard error of the mean (1σ)

$$\varepsilon_{sem}^2 = 1/[\Sigma_n 1/\varepsilon_n^2] \quad (5)$$

as a measure of the precision of the results. The second is the error on the estimation of the *mean*

$$\varepsilon_{std}^2 = [\Sigma_n (v_n^2/\varepsilon_n^2) - (\Sigma_n v_n/\varepsilon_n^2)^2/\Sigma_n (1/\varepsilon_n^2)]/ (M-1)[\Sigma_n(1/\varepsilon_n^2)] \quad (6)$$

obtained from the standard deviation divided by the square root of (M-1), the effective number of samples (microwindows). To account for the different weighting of tho microwindows, M is determined through,

$$M = [\Sigma_n (1/\varepsilon_n)]^2/[\Sigma_n 1/\varepsilon_n^2]. \quad (7)$$

This effective M is smaller than the actual number of microwindows except In the case where the weights are the same. The reported precision error is taken as the larger of these two estimates. In many cases Eqs. 5 and 7 given quite similar results, giving confidence that the final precision error estimate is appropriate.

Processing Methodology

There have been three major versions of the ATMOS data, reflecting the increasing sophistication of the retrieval methodology. The evolution demonstrates the price of certain simplifying assumptions. The three versions are distinguishable by the final processing date: data processed prior to l October 1994 (version 0), data processed prior to 14 December 1994 (version 1) which was widely used in evaluations of measurements made from the Upper Atmospheric Research Satellite (UARS), and data processed prior to 15 April 1995 (version 2) presented In the accompanying letters in this issue.

In early, 1995, the ATMOS data set was revised to address limitations of the version 1 data. Three new elements were added to the process: (a) a final pressure sounding was performed using the version 1 temperature profile to insure that the derived tangent pressures were consistent with the expected mean stratospheric CO_2 volume mixing ratio profile of 350 parts per million by volume (ppmv) *in* 1994, (b) improved low altitude tangent pressure determination (through the definition of new microwindows), and (c) the spectroscopic precision reported as the retrieval precision was re-defined to be more consistent with the random errors in the retrieval process (Eq. 3). The precision of the tangent pressure soundings ss functions of pressure are illustrated in Figure 1; the variation between the optical filters reflects differences in the spectroscopy and number of microwindows at each pressure level. The fractional pressure error ranges between 0.5% and 9%, with the best results typically in the pressure range between 100 and 1 mbars (approximately 18 to 48 ton altitude). Below 100 mbars the errors increase, but are still quite acceptable at 300 mbars (approximately 8 km); in several filters there is a region around 50 km where the number of usable features is Insufficient to maintain consistent precision. A careful analysis of the temperature sensitivity demonstrated that the tangent pressures were not statistically biased, In contrast, subsequent to the release of the version 1 data set inconsistencies In the derivation of pressures with the simultaneous pressure-temperature algorithm led to the conclusion that the version 1 constituent profiles could be locally biased by as much as 8-15%. An Improved pressure-temperature retrieval algorithm was evaluated and found to be capable of converging to a stable answer with a retrieval error of less than 0.3K and a precision of 0.5-1K and confirmed the validity of the tangent pressures derived in the version 2 data set. Mean differences between version 2 data and profiles derived with pressures and temperatures from the Improved algorithm were demonstrated to be less than 2-3%, which is modest with respect to the measurement precisions (typically 2-10% for many gases.).

Error Budget

The version 2 data set has been released to the general science community and utilized In the accompanying letters. Single profile precision ranges are given in Table l for each of the gases routinely profiled from the ATMOS spectral database. For the minor and trace gases with well isolated spectral features (CO_2, O_3, N20, CH_4, H_2O, HCl, and HP) where many microwindows may be combined the precision is typically less than 10%. Retrievals of profiles of the chlorofluorocarbons (CCl_3F and CCl_2F_2) with broadband spectral features that are minimally overlapped by features of other gases yield small precision estimates due to the large amount of spectral information. At the other extreme are species such as HNO_3, N_2O_5, $CHClF_2$, and $ClONO_2$ which require pre-retrieval of 1-6 interfering species. In such cases, the residuals are dominated by interferences and lead to large precision estimates. As illustrated in Figs. 2-4, if the profiles are sharply peaked then the error estimates will tend to 100% at the top and bottom of the profiles, indicating the full range of measurable signal. N_2O_5 is a special case, since the diurnal variation is sufficiently large that sunset retrievals typically have an uncertainty of 16-25%, while the sunrise measurements sampling a much larger amount of gas along the line of sight have smaller uncertainties (note that, the only tropical sunrise data obtained by ATMOS was during the 1992 ATLAS.] mission).

Tangent pressure errors are included in the precision estimates (column 2) in quadrature with the retrieval precision for each constituent (Eqs. 3, 5-7). Approximate altitude ranges given in Table 1 (column 2) correspond to altitude limits between which reasonable results (column 3) are obtained. Accuracy ranges, based on the combined systematic uncertainties in spectroscopic parameters [Brown *et al.*, 1995] of the retrieved constituent and the CO_2 transitions used for pressure sounding, are given in Table 1 (column 5) to indicate the total uncertainties (random and systematic) for comparison with other measurements and model calculations.

Both long-lived and reactive trace gases are expected to have minimal spatial variability in tho tropics and consequently, the zonal average standard deviation of measurements at tropical latitudes may be used to assess the precision of the measurements relative to the expected natural variability of 5-8% at most altitudes between 15 and 50 ion (column 4). For the trace gases, the standard deviation is typically comparable to the total precision, indicating that the precision estimate and the measurement variance are in reasonable agreement. The standard deviations for the minor and source gases are sufficiently small that comparisons with other experiments should allow an assessment of the accuracy of the measurements. For some gases ($ClONO_2$)the zonal standard deviation is actually less than the reported Precision, indicating that the later Is actually an overestimate (resulting from the inadequacy of the pre-retrieval of interfering spectral lines in this case).

Table 1: ATMOS Version 2 Data Precision and Accuracy

Species	Altitude Range (km)	Est. Prec. (%)	Zonal s.t.d. (%)	Est. Acc. %
O_3	10-77	·2-5	2-8	+ -
N20	10-s3	3-5	2.10	5
CH4	10-65	3-5	3-14	5
HN03	15-40	3-6	3-10	16
H_2O	10-83	5-7	2-8	6
HCl	13-53	5-8	1-5	s
HP	12-55	5-10	1-10	s
NO	18-100	10-20	1-10	5
N02	15-48	4-10	i-lo	6
CCl_3F	IO-29	3-s	4-15	11
CCl_2F_2	10-31	395	2-1o	9
$CHClF_2$	10-31	12-25	3-1o	11
$ClONO_2$	t 6--39	40	3.20	20
N_2O_5 (ss)	21-40	16-25	8-3S	16
N_2O_5 (sr)		3-s	12.20	16
SF_6	10-27	7-20	2-1s	11
OCS	10-24	1s-20	2-7	9
HCN	10-29	7-18	2-10	6
HDO	10.40	20.30	3-1s	7
$H_2{}^{17}O$	10-49	12-20	S-IS	7
$H_2{}^{18}O$	18-65	13-25	3.12	7
CH_3D	10.35	16-23	3-7	7
CO	is-loo	S-20	3.1s	5
HNO_4	16-40	30-60	[0-30	20
CCl_4	10-27	7-15	4.1s	20
C2H2	10-24	>50	>50	7
C_2H_6	10-24	25	2s	11
CH_3Cl	10-27	>50	5-20	11
CF_4	10-58	20-40	2 - 7	11

Conclusions

The methodology and accuracies of the ATMOS data processing have been summarized and evaluated. The reported error budget for version 2 data is presented and evaluated, with the intent of describing the quality and limitations of the database. Vertical error profiles highlight rho range over which retrievals produce reasonable results, and the regions where the uncertainty in the measurement process dominates the result. A summary error budget provides a simple set of guidelines to the relative quality of ATMOS measurements trace gas burdens, which should permit users of the ATMOS data to focus on measured features of the atmosphere *rather than* features of the ATMOS retrieval process. The expected accuracy of the spectroscopic database provides a similar guideline for comparing ATMOS profiles with the results from other experiments.

Acknowledgments. Research at the Jet Propulsion Laboratory (JPL), California Institute of Technology, is performed under contract to the National Aeronautics and Space Administration (NASA). Research at the University of Liège was partially supported by the Belgian Global Change Program through the SSTC, Brussels. The authors greatly appreciate the careful scientific and editorial comments of several colleagues, especially those of R. J. Salawitch.

References

Abrams, M. C., *et al.*, A practical example of the correction of Fourier transform spectra for detector nonlinearity, *Appl. Opt.*, 33, 6307-6314, 1994.

Abrams, M. C., *et al.*, Pressure sounding of the middle atmosphere from ATMOS solar occultation measurements of atmospheric CO_2 absorption lines, *Appl. Opt.*, in press, 1996a.

Abrams, M. C., *et al.*, Remote sensing of the Earth's atmosphere from space with high resolution Fourier transform spectroscopy: development and methodology of data processing for the Atmospheric Trace Molecule Spectroscopy experiment, submitted, *Appl. Opt.*, 1996b.

Abrams, M. C., *et al.*, An evaluation of stratospheric ozone observed by the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment during April 1992, *J. Geophys. Res. (Atmospheres)*, in preparation, 1996c.

Brown, L. R. *et al.*, The 1995 Atmospheric Trace Molecule Spectroscopy (ATMOS) Linelist, submitted, *Appl. Opt.*, , 1995.

Gunson, M. R., *et al.*, An overview of the ATMOS experiment during the ATLAS Space Shuttle missions of 1992-4, submitted, *Geophys. Res. Lett.*, , 1496.

Hedin, A. E., Extension of the MSIS thermosphere model into the middle and lower atmosphere, *J. Geophys. Res.*, 96, 1159-1172, 1991.

Norton, R. H., and C. P. Rinsland, ATMOS data processing and science analysis methods, *Appl. Opt.*, 30, 389-400, 1991.

Stiller, G. P., *et al.*, Stratospheric and mesospheric pressure-temperature profiles from the rotational analysis of CO_2 lines of the ATMOS/ATLAS-1 observations, *J. Geophys. Res.*, 100, 3,107-3,117, 1995.

M. C. Abrams (m.c.abrams@larc.nasa.gov), NASA LaRC MS-475, Hampton, VA, 23681, USA

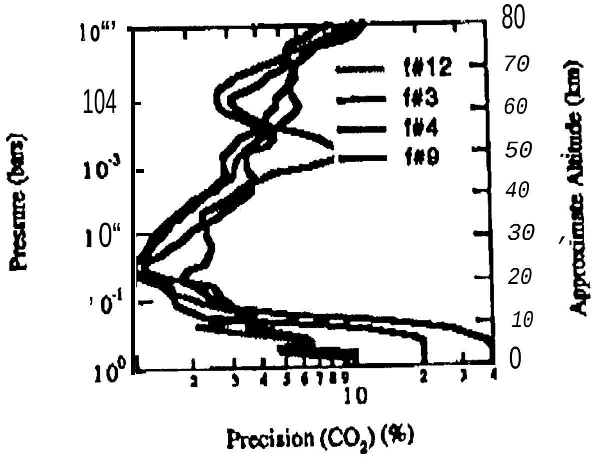

Figure 1. Tangent pressure precisions (viewing geometry) for the four primary optical filters used by ATMOS (f#12: 625-1450 cm^{-1}, f#3: 1580-3450 cm^{-1}, f#4: 3100-4800 cm^{-1}, f#9: 625-2450 cm^{-1}).

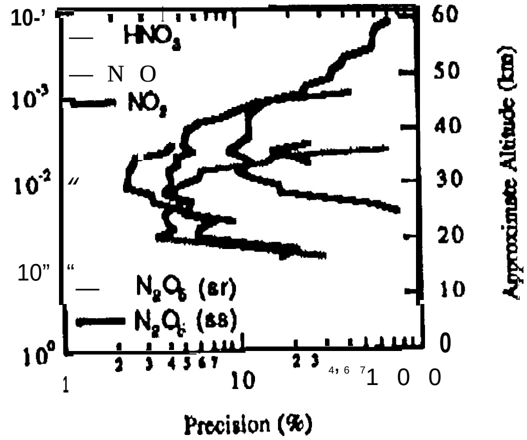

Figure 3, Precisions for odd nitrogen species. Notice the dramatic difference in dinitrogen pentoxide precisions depending on the time of day.

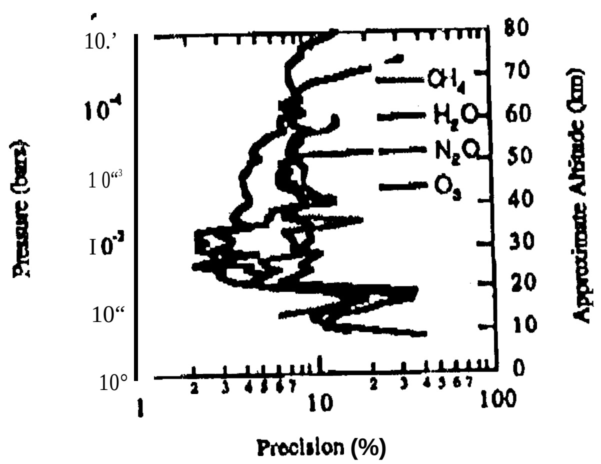

Figure 2. Precisions (root sum quart of retrieval precision and tangent pressure precision) for the minor gases.

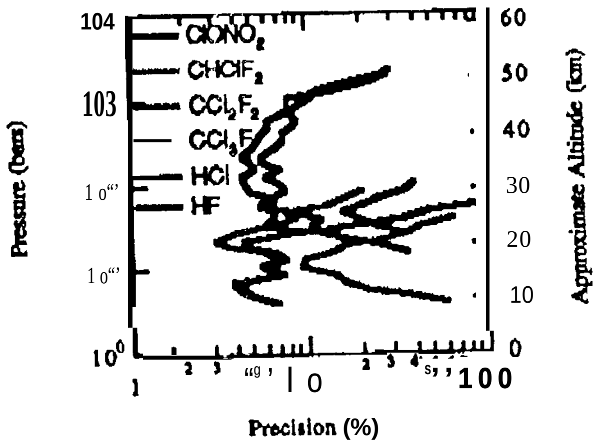

Figure 4. Precisions for chlorine- and fluorine-bearing species including the source gases (CCl_3F, CCl_2F_2, and $CHClF_2$) and reservoir species HCl and HF.